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# RHEOLOGICAL PROPERTIES OF SLIPS BASED ON CLAYS FROM THE MSTERSKOE DEPOSIT

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The results of experimental studies of the rheological properties of slips based on clay obtained from the Msterskoe deposit in Vladimir Oblast' and modified with sheet-glass cullet and soda. The experimental data are evaluated.

***Key words:*** Msterskoe clay, slip, electrolyte, viscosity, thickening factor, rate and mass of slip buildup, electrokinetic potential, pH.

Vladimir Oblast' possesses significant reserves of raw materials, including clays with different chemical and mineralogical compositions, which are mainly used for the production of building brick. The best clays come from the Msterskoe deposit and are used at the Mstera Ceramic Wall Materials Works JSC for the production of high-quality building brick with different shapes and porosity.

The purpose of the present work was to investigate the possibility of using the clays from the Msterskoe deposit for preparing slips for the production of assorted articles.

To study the pouring properties of slips, aside from the Msterskoe clay as the main raw material, sheet-glass cullet was used as an additive to make the articles stronger and top-quality grade B soda was used as an electrolyte.

The chemical composition of the clay is represented by the following oxides (mass fraction, %): $SiO_2$ – 79.78; $Al_2O_3$ – 10.02; $TiO_3$ – 0.595; $Fe_2O_3$ – 3.05; CaO – 1.095; MgO – 0.895; $Na_2O$ – 0.445; $K_2O$ – 1.680 (calcination losses – 3.210). The granulometric composition is represented by the following fractions (mass fraction, %): > 0.06 mm – 36.35; fraction 0.06...0.01 mm – 28.87; 001...0.005 mm – 6.07; 0.05...0.001 mm – 5.43; < 0.001 mm – 23.28.

The chemical composition of the cullet is represented by the following oxides (mass fraction, %): $SiO_2$ – 72.8; $Al_2O_3$ – 1; $SiO_3 \le 0.5$; $Na_2O + K_2O = 13.4$; CaO – 8.7; MgO – 3.6; $Fe_2O_3$ – 0.1 – 0.015.

Before the slip was prepared the clay was granulated into small pieces, ground in a mortar and passed through a No. 0634 sieve (116 openings/cm$^2$); the cullet was ground in a ball mill for 2 h and them passed through a No. 041 sieve (320 openings/cm$^2$). The materials were weighted in the ratios indicated in Table 1.

A composition with mass 500 g comprised of water, clay and cullet was taken as 100%. The amount of soda was taken as a percentage of the amount of the solid phase of the slip and added above 100%. The mixture of raw materials was mixed with distilled water added in a definite percentage. The composition prepared was allowed to stand for 24 h. Before testing, the slip was remixed for 10 – 15 min.

The investigations consisted in determining the basic rheological properties of the slips: viscosity, maximum shear stress, thickening factor, rate of build-up and mass of the slip, electrokinetic potential and pH. These properties were determined by standard methods [1].

**TABLE 1.** Experimental Slip Compositions

| Composition | Content, wt.% | | | | | | |
|---|---|---|---|---|---|---|---|
| | Water | Clay | Cullet | Soda* | | | |
| | | | | 1 | 2 | 3 | 4 |
| I | 45 | 85 | 15 | 0.60 | 0.45 | 0.3 | 0.15 |
| II | 40 | 85 | 15 | 0.60 | 0.45 | 0.3 | 0.15 |
| III | 37 | 85 | 15 | 0.45 | 0.60 | 0.8 | 1.00 |

* Above 100%.

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**TABLE 2.** Efflux Time and Relative Viscosity of the Slips

| Index | Composition | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | | | | II | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Efflux time $\tau_{0.5}$ | 4.25 | 4.24 | 4.08 | 3.80 | 15.60 | 5.20 | 5.33 | 4.87 |
| Relative viscosity $\eta_0$ | 1.25 | 1.24 | 1.20 | 1.14 | 4.59 | 1.53 | 1.57 | 1.43 |

The relative viscosity $\eta_0$ of the clay suspensions was determined with an Engler viscometer by dividing the efflux time for 100 cm$^3$ of slip by the efflux time of the same amount of water (the water efflux time $\tau_{H_2O} = 3.4$ sec).

The results obtained for the slip efflux times and the computed values of the relative viscosity are presented in Table 2.

The values of the relative viscosity for the composition III are not presented in Table 2; these slips did not efflux through the opening of the Engler viscometer because of their high density. As one can see in Table 2, there is no definite variation of $\eta_0$ for composition I or II but $\eta_0$ is higher for composition II.

The computational results for the thickening factor $K$, viz., the ratio of the fluidity of a slip kept at rest for 30 min ($\tau_{30}$) after mixing to the fluidity after mixing and keeping at rest for 30 sec ($\tau_{0.5}$), are presented in Table 3.

The values of the relative viscosity $\eta_0$, plastic viscosity $\eta_p$ and thickening factor K for the experimental compositions are presented in Fig. 1 ($\eta_p$ is a conditional quantity, showing the fraction of the viscous resistance of the slip arising on thickening (for certain loads).

Thus, for slip with moisture content $W = 40\%$ (Fig. 1*b*) all viscosity indices increase with electrolyte content increasing from 0.15 to 0.6%, while for slip with moisture content $W = 45\%$ (Fig. 1*a*) the thickening factor decreases for the indicated electrolyte contents.

As the electrolyte content in slip with moisture content $W = 37\%$ (Fig. 1*c*) increases from 0.15 to 0.6% the relative viscosity and plastic viscosity increase while the thickening factor decreases.

**TABLE 3.** Calculation of the Thickening Factor

| Index | Composition | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | | | | II | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| $\tau_{30}$ | 4.40 | 4.60 | 4.28 | 4.20 | 32.60 | 6.80 | 6.60 | 5.20 |
| $\tau_{0.5}$ | 4.25 | 4.24 | 4.08 | 3.80 | 19.90 | 5.27 | 5.40 | 4.60 |
| $K$ | 1.03 | 1.08 | 1.05 | 1.105 | 1.64 | 1.29 | 1.22 | 1.13 |

For electrolyte content from 0.15 to 0.6% the slip with moisture content $W = 37\%$ was very dense and the body largely comprised a paste. For this reason the coefficient of plastic viscosity could be determined only for electrolyte content 0.45 – 1.0%.

The behavior of the coefficient of plastic viscosity of all experimental compositions as a function of the percentage content of electrolyte was unusual. This is explained by the structure of the clayey micelles, which was examined in detail in [2]. In this work the rheological properties of the slip are explained by the influence of the electrolyte concentration on the amount of free and bound water in the slip, i.e., in order to prepare the slip it is necessary not only to determine the optimal moisture content of a suspension but also to refine the amount of electrolyte introduced into the suspension in order for free water to accumulate. As follows from the experimental data obtained, for Msterskoe clay the moisture content of slip must be in the range 40 – 45% with electrolyte content 0.45%.

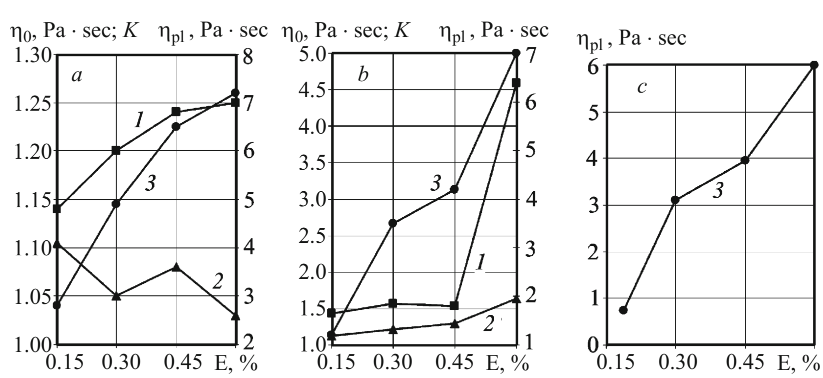


**Fig. 1.** Effect of the content (by weight) of electrolyte E on the rheological properties with different moisture content of the slip: *a*) moisture content 45%; *b*) moisture content 40%; *c*) moisture content 37%; *1*) relative viscosity of slip $\eta_0$; *2*) thickening factor $K$; *3*) coefficient of plastic viscosity $\eta_p$.

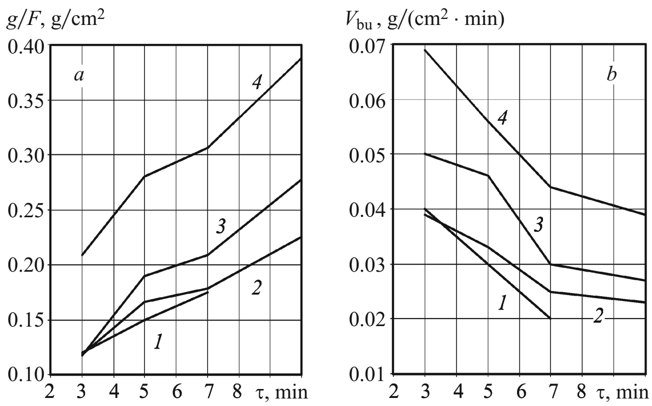


**Fig. 2.** Slip mass (*a*) and buildup rate (*b*) with moisture content $W = 45\%$ versus the buildup time: *1*) composition I-1; *2*) composition I-2; *3*) composition I-3; *4*) composition I-4.

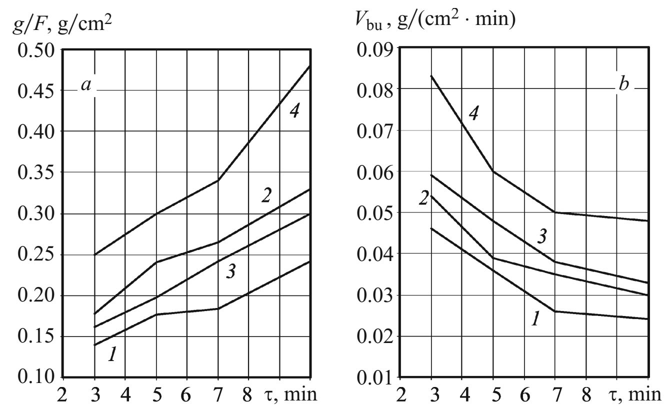


**Fig. 3.** Slip mass (*a*) and buildup rate (*b*) with moisture content $W = 40\%$ versus the buildup time: *1*) composition II-1; *2*) composition II-2; *3*) composition II-3; *4*) composition II-4.

The buildup rate and mass for the experimental compositions were determined from the results of an experiment based on the immersion of standard gypsum rods into the slip for 3 – 10 min [1]. According to the method of [1], the mass buildup was determined as the ratio of the mass $g$ of a dry layer to the surface area $F$ of the rod.

The experimental and computational results are presented in Tables 4 and 5.

The plots displayed in Figs. 2 – 4 were constructed using the data in Tables 4 and 5.

It follows from Figs. 2 – 4 that as the mass increases the buildup rate decreases for all experimental compositions.

The electrokinetic potential of the slips was determined by the method of electrophoretic displacement of the visible boundary of the system clayey slip – contact electrolyte KCl for constant voltage 100 V in the Burton apparatus [3]. The distance between the electrodes was equal to 24.5 cm for the composition I-1 and 24.8 cm for compositions I-2 and I-3. For all other compositions the ξ-potential could not be determined because of their high density. The experimental results are given in Table 6, where R and L are the right- and left-hand bends of the vessel, respectively.

The data required to calculate the electrokinetic potential were determined from a plot of the dependence $S = f(\tau)$. This

**TABLE 4.** Mass Buildup for the Experimental Compositions $g/F$, g/cm$^2$

| Rod No. | Composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | | | | II | | | | III | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 7 | 0.120 | 0.118 | 0.117 | 0.209 | 0.139 | 0.178 | 0.162 | 0.25 | 0.129 | 0.208 | 0.146 | 0.140 |
| 2 | 0.150 | 0.166 | 0.190 | 0.280 | 0.177 | 0.240 | 0.197 | 0.30 | 0.193 | 0.225 | 0.198 | 0.196 |
| 6 | 0.175 | 0.178 | 0.209 | 0.306 | 0.183 | 0.265 | 0.242 | 0.34 | 0.195 | 0.260 | 0.230 | 0.210 |
| 4 | – | 0.225 | 0.277 | 0.388 | 0.242 | 0.330 | 0.300 | 0.48 | 0.235 | 0.328 | 0.266 | 0.260 |

**TABLE 5.** Mass Buildup Rate for the Experimental Compositions $V_{bu}$, g/(cm$^2$ · min)

| Rod No. | Composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | | | | II | | | | III | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 7 | 0.04 | 0.039 | 0.050 | 0.069 | 0.046 | 0.059 | 0.054 | 0.083 | 0.043 | 0.069 | 0.0490 | 0.047 |
| 2 | 0.03 | 0.033 | 0.046 | 0.056 | 0.036 | 0.048 | 0.039 | 0.060 | 0.036 | 0.045 | 0.0390 | 0.039 |
| 6 | 0.02 | 0.025 | 0.030 | 0.044 | 0.026 | 0.038 | 0.035 | 0.050 | 0.027 | 0.037 | 0.0325 | 0.029 |
| 4 | – | 0.023 | 0.027 | 0.039 | 0.024 | 0.033 | 0.030 | 0.048 | 0.023 | 0.033 | 0.0270 | 0.026 |

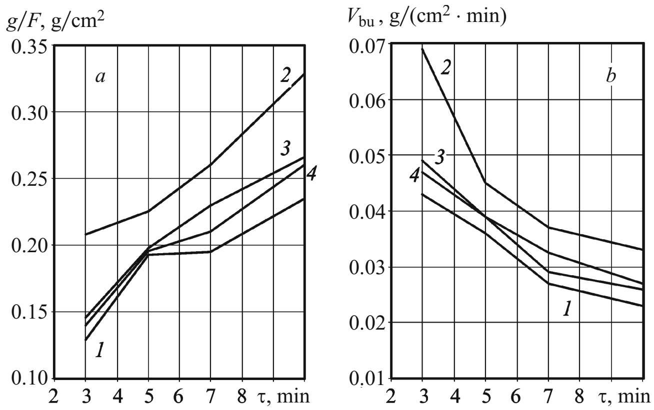


**Fig. 4.** Mass and buildup rate of slip with moisture content $W = 37\%$ versus the buildup time: *a*) mass; *b*) buildup rate; *1*) composition III-1; *2*) composition III-2; *3*) composition III-3; *4*) composition III-4.

function was constructed from the data in Table 6 and is displayed in Fig. 5.

The value of the electrokinetic potential was determined as the arithmetic mean of the forward and return courses. The computational results are presented in Table 7.

An IV74 ion meter with glass and silver chloride electrodes in standard solutions with pH = 1.68, 6.86 and 9.18 was used to determine the pH.

A plot of the pH versus the content (by weight) of the electrolyte is presented in Fig. 6.

As one can see from Fig. 6, for the experimental slips the pH of the slip increased with increasing electrolyte content. Likewise, the pH decreased with increasing moisture content of the slip.

The work presented here makes it possible to conclude that the rheological properties of the clay studied are adequate for the production of diverse ceramic articles by slip casting. This will make it possible to expand the range of products produced by Mstera Ceramic Wall Materials Works JSC, including art ceramic as well as thin-layer samples for

**TABLE 6.** Measurements of the Movement of the Slip – Contact Electrolyte Interface

| Distance traversed by the slip $S$, cm | Time τ, sec | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0 | 120 | 240 | 360 | 480 | 600 | 720 | 840 |
| Composition I-1 | | | | | | | | |
| Forward course: | | | | | | | | |
| $L_1$ | 1 | 1.2 | 1.3 | 1.70 | 2.0 | 2.25 | 2.4 | 2.5 |
| $R_1$ | 1 | 0.9 | 0.8 | 0.75 | 0.7 | 0.70 | 0.7 | 0.7 |
| Return course: | | | | | | | | |
| $L_2$ | 2.7 | 2.60 | 2.40 | 2.3 | 2.0 | 1.75 | 1.5 | 1.20 |
| $R_2$ | 0.7 | 0.75 | 0.75 | 0.8 | 0.8 | 0.80 | 0.85 | 0.95 |
| Composition I-2 | | | | | | | | |
| Forward course: | | | | | | | | |
| $L_1$ | 1.8 | 2.15 | 2.50 | 3.2 | 3.4 | 3.60 | 3.8 | 3.95 |
| $R_1$ | 1.8 | 1.75 | 1.75 | 1.7 | 1.7 | 1.65 | 1.65 | 1.65 |
| Return course: | | | | | | | | |
| $L_2$ | 3.95 | 3.80 | 3.7 | 3.60 | 3.4 | 3.15 | 2.8 | 2.5 |
| $R_2$ | 1.65 | 1.75 | 1.8 | 1.85 | 1.9 | 1.95 | 2.1 | 2.3 |
| Composition I-3 | | | | | | | | |
| Forward course: | | | | | | | | |
| $L_1$ | 1.75 | 2.00 | 2.30 | 2.70 | 3.1 | 3.7 | 3.8 | 3.9 |
| $R_1$ | 1.80 | 1.75 | 1.75 | 1.75 | 1.7 | 1.7 | 1.7 | 1.7 |
| Return course: | | | | | | | | |
| $L_2$ | 3.9 | 3.7 | 3.30 | 3.00 | 2.8 | 2.45 | 2.2 | 2.0 |
| $R_2$ | 1.7 | 1.7 | 1.75 | 1.75 | 1.8 | 1.85 | 1.9 | 2.0 |

**TABLE 7.** Values of the Electrokinetic Potential of the Slip

| Composition | Displacement of the slip boundary $S$, cm | | Electrokinetic potential ξ, V | | |
|---|---|---|---|---|---|
| | Forward course | Return course | Forward course | Return course | Average value |
| I-1 | 2.00 | 1.70 | 0.081 | 0.069 | 0.075 |
| I-2 | 2.25 | 1.90 | 0.088 | 0.074 | 0.081 |
| I-3 | 2.45 | 1.95 | 0.096 | 0.076 | 0.086 |

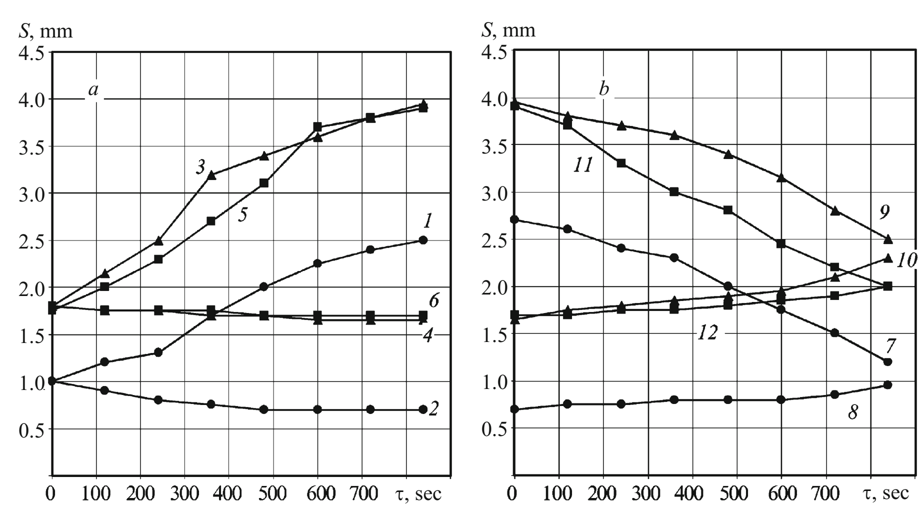


**Fig. 5.** Displacement of the slip – contact electrolyte interface versus time: *a*) forward course; *b*) return course; *1*) I-1 ($R_1$); *2*) I-1 ($L_1$); *3*) I-2 ($R_1$); *4*) I-2 ($L_1$); *5*) I-3 ($R_1$); *6*) I-3 ($L_1$); *7*) I-1 ($R_2$); *8*) I-1 ($L_2$); *9*) I-2 ($R_2$); *10*) I-2 ($L_2$); *11*) I-3 ($R_2$); *12*) I-3 ($L_2$).

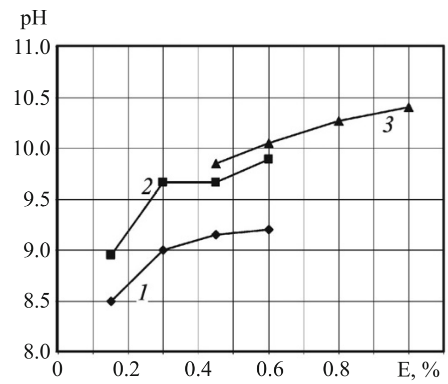


**Fig. 6.** pH versus the content (by weight) of the electrolyte E: *1* ) composition I; *2* ) composition II; *3* ) composition III.

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